·PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

Manufacture of Fluorocarbons

We, ALLIED CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 61 Broadway, New York 6, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

THIS INVENTION relates to processes for the production of fluorocarbons by fluorinating aliphatic halocarbons.

It has been found that substantially anhydrous dichromium trioxide, Cr_2O_3, catalyses the fluorination of certain aliphatic halocarbons with anhydrous hydrogen fluoride to form compounds having higher fluorine contents, and that the dichromium trioxide possesses properties which effect high yield metathetical exchange or organically bound non-fluorine halogen of the starting material for fluorine contained in the hydrogen fluoride.

According to the invention fluorocarbons are made by heating a halogenated straight chain saturated C_1—C_4 aliphatic hydrocarbon containing at least one carbon atom carrying at least two halogen atoms of which one at least is chlorine or bromine, and containing no element other than carbon, fluorine, chlorine, bromine and hydrogen in the gas phase with gaseous substantially anhydrous hydrogen fluoride at a temperature of 225—650° C. in the presence of a catalyst consisting of dichromium trioxide and obtained by precipitating hydrous chromic oxide from an aqueous solution of a trivalent chromium salt and subsequently heating it to 300—400° C. for not less than one hour.

The reactions involved may be represented by

$$RX + HF \rightarrow RF + HX$$
$$R^1X + 2HF \rightarrow R^1F_2 + 2HX$$
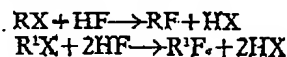
where X represents chlorine or bromine, and R is a halohydrocarbon radical which may contain varying amounts of fluorine, chlorine and bromine.

The saturated halogenated straight chain C_1—C_4 aliphatic hydrocarbon compounds preferably contain one or three carbon atoms. The invention particularly provides an advantageous route for the manufacture of carbon tetrafluoride, and for this purpose the starting material will contain a single carbon atom. Thus the starting material may be a perhalogenated methane containing at least one chlorine atom, all the other halogen atoms being either fluorine or chlorine, and the fluorination temperature is 400—550° C, and tetrafluoromethane is produced. In addition to the starting materials indicated in the appended Examples, the compound 2-chloro - 3,3 dichloroheptafluorobutane (CF_3 $CFClCCl_2CF_3$) may be particularly mentioned.

The anhydrous dichromium trioxide catalysts are made by a specific heat treatment of hydrous chromic oxides derived as precipitates from aqueous solutions of trivalent chromium salts such as chromium nitrate, chloride, and sulphate. While the hydrous chromic oxides may be precipitated by adding bases such as sodium and potassium hydroxides to the chromic salt solutions the preferred catalysts are those derived from hydrous chromic oxides precipitated by means of ammonia, e.g. as ammonia gas or aqueous ammonium hydroxide. A satisfactory method for making such a hydrous oxide is to add an aqueous solution of ammonia to a heated aqueous solution of a trivalent chromium salt, preferably the nitrate ($Cr(NO_3)_3.9H_2O$, until the solution is approximately neutral, at about pH 7. The resulting solution may be boiled for a few minutes and filtered while hot. The hydrous chromic oxide precipitate recovered on filtration may be hot water-

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washed to leach out ammonium nitrate and any other water-soluble impurities, and then converted to the catalyst of the invention by heat treatment at temperatures not higher than about 400° C., preferably after a preliminary drying effected in any suitable way such as by heating under vacuum or in an inert gas stream, or by heating in any equipment provided with facilities for steam escape. In one of the better methods the hydrous chromic oxide is dried at a temperature of about 100—200° C. to remove most of the combined water, and the partially dehydrated oxide is then granulated to about 4 to 20 mesh (apertures 4.7 to 0.8 mm.) or pressed to pellets, e.g. about 3 mm. in diameter and 10 mm. long. The sized material is then subjected to heat treatment for a substantial period of time at a temperature of about 300—400° C.

In all embodiments of the invention, particularly when the chromic oxide has been precipitated (with ammonia), it is preferred to subject the chromic oxide to the heat treatment in a suitable vented heating chamber, i.e. in an atmosphere consisting of water vapour and optionally an inert gas, for at least two hours, especially two to four hours and until the gases leaving the heat treater contain no water. This heat treatment, in addition to effecting an unusually thorough degree of dehydration, imparts to the catalytic material the properties to which are attributable its fluorination characteristics.

Although this is not preferred, the dichromium trioxide catalysts may be used in supported form, i.e. supported on inert refractory material such as silica, fused alumina chips, or calcium or magnesium fluoride. A supported catalyst may be prepared, for example, by soaking fused alumina 4—8 mesh (apertures 4.7 to 2.4 mm.) chips in a saturated solution of chromic nitrate, filtering, drying and heat-treating at 300—400° C., as above. Alternatively, a supported catalyst may be made by coprecipitating chromic hydroxide and a refractory material such as calcium or magnesium fluoride and, after filtering, subjecting the precipitate to drying and heat treatment as above. In making supporting catalysts, the reactants may be used in proportions such that the catalytic materials contain 1—60%, preferably 2—45%, by weight of Cr_2O_3.

Preferably, however, the catalysts are used in unsupported but sized form, i.e. in granular or pelleted form. Catalysts made as described above by precipitation with ammonia followed by the heat treatment at 300—400° C. are substantially amorphous, and have a crystallite size, as determined by X-ray diffraction. A further characteristic of these unsupported catalysts is their relatively high surface area, which is generally at least 5m²/g. and usually above 50m²/g., as determined by the standard nitrogen adsorption method described by Emmett and Brunauer, Journal American Chemical Society, Vol. 56, 35 (1934), using the method of calculation of Harkins and Jura, Journal American Chemical Society, Vol. 66, 1366 (1944).

Any suitable chamber or reactor tube equipped for metered introduction of reactants and constructed of inert material may be employed for carrying out the reaction, provided the reaction zone is of sufficient length and cross-sectional area to accommodate the amount of catalyst necessary to provide adequate gas contact area and at the same time to afford sufficient free space for passage of the gas mixture at an economical rate of flow. Materials such as nickel, graphite, "Inconel" (a Trade Mark) and other materials resistant to hydrogen fluoride may be used. The reactor tube may be externally heated, as by electrical resistance heaters.

The process of the invention in general may be carried out by introducing a gaseous mixture of the reactants into a reaction zone containing the catalyst, and heating the mixture in the zone at the temperatures indicated above for a time sufficient to convert an appreciable amount of the halocarbon starting material into a higher fluorinated compound, withdrawing the gaseous products from the zone, and recovering the fluorinated material from them. Atmospheric pressure is preferred, but the reaction may, if desired, be carried out at superatmospheric or subatmospheric pressure.

The reaction temperature is maintained at or above the level at which fluorination of the particular starting material begins to take place in the presence of gaseous hydrogen fluoride and dichromium trioxide catalyst. Some fluorination may be noted at temperatures as low as about 225° C., but the reaction proceeds at a more satisfactory rate, and fluorination will generally be more complete, at temperatures upwards of about 250° C. Temperatures as high as about 650° C. can be used, although to guard against decomposition of starting material and products, temperatures higher than about 600° C. are usually not employed. Thus, the preferred temperature range is 250—600° C. Temperature variations within this range, along with variations in the mol ratio of hydrogen fluoride to halocarbon starting material and the particular halocarbon used, determine what products will be formed, and in what relative amounts. For making carbon tetrafluoride, temperatures in the range 400—550° C. are preferred.

The molar ratio of hydrogen fluoride to halocarbon (i.e. total organics charged) depends to a considerable extent on the amount of fluorine, if any, contained in the halocarbon and the amount of fluorine desired in the product. Generally, if a highly fluor-

inated product is desired, and the halocarbon contains no fluorine or only a small proportion and contains a relatively large number of chlorine and/or bromine atoms to be replaced, correspondingly large amounts of the hydrogen fluoride are introduced into the reactor. One mol of hydrogen fluoride for each atom of chlorine or bromine to be substituted is the theoretical requirement. It is generally desirable to maintain the mol ratio of hydrogen fluoride to total organic starting material sufficiently low to ensure a high percentage utilisation of the fluorine in the hydrogen fluoride, so simplifying or avoiding the potentially difficult problem of recovering unchanged hydrogen fluoride from the product mixture; recycling of unreacted halocarbon is more practicable than recovery of unreacted hydrogen fluoride. In view of the permissibly wide compositional variations of both starting materials and end products, the mol ratio of hydrogen fluoride to organic starting material may also vary widely, but in general it will lie in the range 1:1 to 10:1.

The contact time of the reactants with the catalyst may also vary considerably. Short contact time tends to form products of relatively low fluorine content, and vice versa. The contact time may vary from one to 100 or more seconds, but is ordinarily not less than about 3 seconds, and preferably in the range 5—50 seconds. In a particular operation, the rate of flow of the reactants in the reaction zone is dependent upon variables such as the scale of operation, the quantity of catalyst in the reactor, the particular organic starting material used, the temperature, the product to be made, and the specific apparatus employed, and is best determined empirically in each case together with the temperature and mol ratio of the reactants to be employed, by means of test runs.

The fluorinated product may be recovered by conventional means. For example, the gas stream which has left the reaction zone, after removal of acidic constituents and drying, may be condensed and the condensate fractionally distilled. For experimental purposes the identity and amount of product in the gas stream may be determined by fractional distillation and/or conventional infrared or other analytical techniques. The gaseous product may be condensed in a vessel maintained at a temperature substantially below the boiling point of the lowest boiling material present, e.g. by indirect cooling of the gas in a bath of, for example, acetone/solid carbon dioxide or liquid nitrogen. Substantially pure product may be recovered by fractional distillation of condensates so obtained, and unreacted halocarbon starting material and/or under-fluorinated compounds recycled to a subsequent operation.

The following Examples illustrate the invention. In all of the Examples "conversion" denotes mols of starting material consumed divided by mols of starting material fed multiplied by 100. Yields are on the basis of starting material consumed, i.e. mols of product divided by mols of starting material consumed, multiplied by 100.

Except as indicated, the dichromium trioxide catalysts employed in all runs were prepared by adding about 530 g. of commercial grade high purity. $Cr(NO_3)_3.9H_2O$ and 500 g. of 28% aqueous ammonium hydroxide with stirring to 2000 ml. of water heated to about 90° C. The resulting precipitated hydrous chromic oxide was filtered, water-washed, preliminarily dried by heating at about 125° C., and pelleted to about 6—10 mesh (3.3 to 1.6 mm.) pellets. These hydrous chromic oxide pellets (about 300 cc.) were charged into a nickel tubular reactor 91 cm. long and 2.5 cm. in internal diameter, mounted in an electrically heated furnace equipped with means for maintaining in the reactor the temperatures stated. The inlet end of the reactor was provided with facilities for metered introduction of vaporous reactants, and the outlet end was connected to the inlet end of a product recovery system. To complete the preparation of the catalyst, the pellets in the reactor were subjected to suitably vented heat treatment at a temperature of 370—400° C. for about four hours, and thereafter until the gas leaving the heater contained no water, to complete the dehydration and to effect the changes to which the high fluorination activity of the dichromium trioxide catalyst is attributable. In all runs, unless otherwise indicated, the gases from the reactor were scrubbed with water to remove hydrogen chloride and hydrogen fluoride, and with dilute caustic soda to remove residual acids. Thereafter, the gas stream was dried by passing it through a calcium chloride tower, and depending upon the boiling points of the organic compounds to be condensed, the dried gas stream was passed into a cold trap refrigerated either by a dry ice/acetone mixture or by a liquid nitrogen bath. The products were analysed and identified by conventional procedures including infrared spectrum analysis.

EXAMPLE 1

After the production of the catalyst, the temperature in the reactor was lowered to about 300° C. and was so maintained throughout the run. During about 3 hours, 135 g. (0.72 mols) of 1,1,1-difluorochloro-2,2,2 - dichlorofluoroethane and 30 g. (1.5 mols) of anhydrous hydrogen fluoride were simultaneously metered into the reactor and through the catalyst bed. The mol ratio of hydrogen fluoride to halocarbon was about

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2:1, and the contact time in the reactor was about 15 seconds. About 140 g. of organic compounds were collected in the cold trap. The water scrubber liquor was titrated for hydrogen chloride, and about 0.327M Cl- was found. The trap condensate was fractionally distilled, and 1,1,2,2 - tetrafluoro-1-2-dichloroethane (CF₂ClCF₂Cl) was recovered in amount indicating a 45% conversion and a 95% yield. After 92 hours of use, when examined by X-ray diffraction, the catalyst was found to be completely amorphous, and had a surface area of 64M²/g.

EXAMPLE 2

During about 4.75 hours, 1.41 mols of dichlorodifluoromethane, and 3.75 mols of anhydrous hydrogen fluoride were metered into the reactor. The mol ratio was about 1:2.7, the temperature was maintained at about 460° C., and the contact time was about 14 seconds. About 115 g. of organic condensate were collected in a liquid nitrogen cold trap. Titration of the scrubber liquor showed a recovery of 2.18 mols Cl-. The condensate was fractionally distilled, and there were recovered about 1.35 mols of carbontetrafluoride b.p. —128° C. and about 0.06 mol of trifluorochloromethane, b.p. 81° C., corresponding to yields of about 96% and 4% respectively.

EXAMPLE 3

During about 6 hours, 1.72 mols of difluorodichloromethane, and 7.5 mols of anhydrous hydrogen fluoride were charged to the reactor containing the same catalyst as in Example 2. The mol ratio was about 1: 4.4, the temperature throughout the run was maintained at about 470° C. and the contact time was about 16 seconds. 137 g. of condensate were recovered in a cold trap. Titration of the scrubber liquor showed a recovery of 3.01 mols Cl-. On fractional distillation of the condensate there were obtained 1.36 mols of carbon tetrafluoride and 0.17 mols of trifluorochloromethane, corresponding to yields of about 79% and 10%.

EXAMPLE 4

During a 4 hour run at a temperature of about 485° C., 1.72 mols of carbon tetrachloride and 7.1 mols of anhydrous hydrogen fluoride were passed into the reactor containing the same catalyst as in Example 1. The mol ratio was about 1:4.4, the contact time about 8 seconds, and about 155 g. or organic compounds were recovered in the trap. Titration of the water scrubber liquor showed a recovery of about 6.72 mols of Cl-. On fractional distillation of condensate there were recovered 1.08 mols of carbontetrafluoride and 0.6 mol of trifluorochloromethane, representing yields of about 63% and about 34%.

EXAMPLE 5

The reactor contained about 420 cc. of catalyst prepared as above. During a 4.75 hour run, at a temperature of about 400° C., 240 g. (2.83 mols) of dichloromethane and 185 g. (9.25 mols) of anhydrous hydrogen fluoride were charged into the reactor. The mol ratio was about 1:3.2, and the contact time was about 13 seconds. 118 g. organic compounds were recovered in the cold trap. Titration of the water scrubber liquor showed a recovery of 3.90 mols Cl-. On fractional distillation of the condensate, 1.21 mols of difluoromethane, b.p. —50° C., and about 0.07 mol of fluorochloromethane (CH₂ClF) b.p. —9° C., were recovered. Conversions were about 43% and 2.5% respectively, and yields were about 54% and 3%.

EXAMPLE 6

During about 4 hours, 215 g. (1.79 mols) of chloroform and 80 g. (4.0 mols) of anhydrous hydrogen fluoride were charged into the reactor containing the same catalyst as in Example 5, the mol ratio being about 2.2:1. The temperature was maintained at about 320° C., and the contact time was about 21 seconds. 145 g. of organic condensate were recovered in the cold trap. Titration of the water scrubber liquor showed a recovery of 2.5 mols of Cl-. On fractional distillation of the condensate, 0.7 mol of dichlorofluoromethane, b.p. 9° C., 0.47 mol of difluorochloromethane, b.p. —40° C., and 0.30 mol of trifluoromethane, b.p. —84° C., were recovered. The respective conversions were about 39%, 27% and 17%, and the yields about 47%, 32% and 20%.

We are aware of Patent Specification 945,017, which claims processes for the preparation of certain fluorinated propanes with hydrogen fluoride, in the presence of a chromium oxide catalyst.

WHAT WE CLAIM IS:—

1. Process for producing fluorinated hydrocarbons, which comprises fluorinating a halogenated straight chain saturated C₁—C₄ aliphatic hydrocarbon containing at least one carbon atom carrying at least two halogen atoms of which one at least is chlorine or bromine, and containing no element other than carbon, fluorine, chlorine, chlorine, bromine and hydrogen by heating it in the gas phase with gaseous substantially anhydrous hydrogen fluoride at a temperature of 225—650° C. in the presence of a catalyst consisting of dichromium trioxide and obtained by precipitating hydrous chromic oxide from an aqueous solution of a trivalent chromium salt and subsequently heating it to 300—400° C. for not less than one hour.

2. Process according to claim 1, in which the fluorination temperature is 250—600° C.

3. Process according to claim 1 or 2,

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in which in the production of the catalyst the precipitate is heated to 300—400° C. for not less than 2 hours.

4. Process according to any one of the preceding claims in which the halogenated hydrocarbon is perchlorofluorinated, and the fluorination temperature is 250—600° C.

5. Process according to any one of claims 1—4, in which the halogenated hydrocarbon contains not more than four carbon atoms.

6. Process according to claim 5, in which the halogenated hydrocarbon contains three carbon atoms.

7. Process according to claim 5, in which the halogenated hydrocarbon contains one carbon atom.

8. Process according to claim 7, in which the halogenated hydrocarbon is a perhalogenated methane containing at least one chlorine atom, all the other halogen atoms being either fluorine or chlorine, the fluorination temperature is 400—550° C., and tetrafluoromethane is produced.

9. Process for producing fluorinated hydrocarbons substantially as hereinbefore described.

10. Carbon tetrafluoride and other fluorinated hydrocarbons obtained by a process claimed in any one of the preceding claims.

J. A. KEMP & CO.,
Chartered Patent Agents,
14 South Square, Gray's Inn,
London, W.C.1.